

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

REC'D 02 OCT 2001

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(PCT Article 36 and Rule 70)

Applicant's or agent's file reference AJM:MG:FP13194	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
International Application No. PCT/AU00/00993	International Filing Date (day/month/year) 21 August 2000	Priority Date (day/month/year) 20 August 1999
International Patent Classification (IPC) or national classification and IPC Int. Cl. ⁷ C09K 3/18, C09D 5/00, 5/08, 5/16, 183/06		
Applicant UNISEARCH LIMITED et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 9 sheets.

3. This report contains indications relating to the following items:

I	<input checked="" type="checkbox"/> Basis of the report
II	<input type="checkbox"/> Priority
III	<input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	<input type="checkbox"/> Lack of unity of invention
V	<input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	<input type="checkbox"/> Certain documents cited
VII	<input type="checkbox"/> Certain defects in the international application
VIII	<input type="checkbox"/> Certain observations on the international application

Date of submission of the demand 14 February 2001	Date of completion of the report 19 September 2001
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer ALBERT S. J. YONG Telephone No. (02) 6283 2160

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/AU00/00993

I. Basis of the report

1. With regard to the elements of the international application:*

- the international application as originally filed.
- the description, pages 1,4-18 , as originally filed,
pages , filed with the demand,
pages 2,3,3a , received on 6 April 2001 with the letter of 5 April 2001
- the claims, pages , as originally filed,
pages , as amended (together with any statement) under Article 19,
pages , filed with the demand,
pages 19-20,22-24, received on 6 April 2001 with the letter of 5 April 2001
pages 21 received on 16 August 2001 with the letter of 16 August 2001
- the drawings, pages 1/1 , as originally filed,
pages , filed with the demand,
pages , received on with the letter of
- the sequence listing part of the description:
pages , as originally filed
pages , filed with the demand
pages , received on with the letter of

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language which is:

- the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

4. The amendments have resulted in the cancellation of:

- the description, pages
- the claims, Nos.
- the drawings, sheets/fig.

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report

V.	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement		
1.	Statement		
	Novelty (N)	Claims 1-42	YES
		Claims	NO
	Inventive step (IS)	Claims 1-42	YES
		Claims	NO
	Industrial applicability (IA)	Claims 1-42	YES
		Claims	NO

2. Citations and explanations (Rule 70.7)

CITATION

D1. JP 10133002

D2. JP 05093170

D3. EP 0381376

D4. EP 0430156

NOVELTY (N) AND INVENTIVE STEP (IS)

Claims 1-42: The claimed invention relates to a modified gel comprising a gel and a particulate material, which modified gel is capable of physically enhancing the surface roughness and hydrophobicity of a substrate. None of the above citations discloses a final treatment step of modifying the intrinsic properties of the gel/particulate mixture.

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Examples of materials on which liquid droplets have high contact angles include water on paraffin, in which there is a contact angle of about 107°. Many applications require a hydrophobic coating with a high contact angle of 5 at least 150°, and preferably at least 165°.

A "gel" is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. The liquid prevents the solid from collapsing, and the solid prevents the liquid from escaping. The solid skeleton can 10 be formed by linking colloidal particles together.

The present inventors have now developed methods for producing materials which, when coated on a surface, render that surface hydrophobic.

15 Summary of the Invention

In a first aspect, the present invention provides a method of forming a material capable of being applied to a surface, the method including the steps of:

- (a) providing precursors capable of reacting to form 20 a gel;
- (b) reacting the precursors together to form the gel;
- (c) adding a particulate material to the gel to form a mixture, the particulate material being capable of chemically bonding with the gel; and
- 25 (d) treating the mixture such that a modified gel is formed in which the particulate material is bound to the gel, and the modified gel is capable of forming a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface
- 30 hydrophobicity, such that water has a contact angle on the surface of at least 150°.

In a second aspect, the present invention provides a method of forming a coating on a substrate, the method

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including steps (a) to (d) of the first aspect of the present invention, and further including the steps of:

(e) applying the modified gel to the substrate; and

(f) treating the applied modified gel such that a

5 coating is formed on the substrate, the coating having a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface hydrophobicity, such that water forms a contact angle of at least 150°.

10 Preferably, the hydrophobic surface defined in either the first or the second aspect of the present invention is such that water forms a contact angle of at least 155° on it. More preferably, the contact angle is at least 160°. Even more preferably, the contact angle is at least 165°.

15 The hydrophobicity of the hydrophobic material when applied to a surface is preferably due to both the chemical properties of the modified gel and physical roughness of the material. It is envisaged that the modified gel of the first aspect of the present invention 20 could be used to make solid materials in a range of possible forms, including bulk materials, thick coatings, and thin films.

The gel functions as a cross-linking agent which binds the particulate material, and attaches the modified 25 gel to the substrate if required. Any known process for forming a gel may be used. Typically, the precursors defined in step (a) of the first and second aspects of the present invention at least include water, a solvent, and a metal alkoxide such as one of the following:

30 -tetramethoxysilane (abbreviated TMOS), $\text{Si}(\text{OCH}_3)_4$

-tetraethoxysilane (abbreviated TEOS), $\text{Si}(\text{OCH}_2\text{CH}_3)_4$;

-titanium tetraisopropoxide, $\text{Ti}(\text{O}-\text{iso-C}_3\text{H}_7)_4$;

-titanium tetramethoxide, $\text{Ti}(\text{OCH}_3)_4$;

- 3a -

- titanium tetraethoxide, $Ti(OC_2H_5)_4$;
- titanium tetrabutoxide, $Ti[O(CH_2)_3CH_3]_4$;
- zirconium n-butoxide, $Zr(O-n-C_4H_9)_4$.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of forming a material capable of being applied to a surface, the method including the steps of:
 - 5 (a) providing precursors capable of reacting to form a gel;
 - (b) reacting the precursors together to form the gel;
 - (c) adding a particulate material to the gel to form a mixture, the particulate material being capable of chemically bonding with the gel; and
 - 10 (d) treating the mixture such that a modified gel is formed in which the particulate material is bound to the gel, and the modified gel is capable of forming a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface hydrophobicity, such that water has a contact angle on the surface of at least 150°.
- 15 2. The method according to claim 1 wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 155°.
- 20 3. The method according to either claim 1 or claim 2 wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 160°.
- 25 4. The method according to any one of the preceding claims wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 165°.
5. The method according to any one of the preceding 30 claims wherein the precursors provided in step (a) include at least water, a solvent, and a metal alkoxide.
6. The method according to claim 5 wherein the solvent

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- comprises an alcohol.
7. The method according to claim 6 wherein the alcohol is selected from the following group:
- methanol;
- 5 ethanol;
- isopropanol;
- and butanol.
8. The method according to claim 5 wherein the solvent is selected from a group comprising: hexane; and
- 10 diethyl ether.
9. The method according to any one of claims 5-8 wherein the metal alkoxide is selected from the following group:
- tetramethoxysilane;
- 15 tetraethoxysilane;
- titanium tetraisopropoxide;
- titanium tetramethoxide;
- titanium tetraethoxide;
- titanium tetrabutoxide;
- 20 zirconium n-butoxide.
10. The method according to any one of the preceding claims wherein step (b) of reacting the precursors together comprises refluxing the precursors for an extended period.
- 25 11. The method according to any one of the preceding claims wherein the particulate material comprises particles having substantially equal diameters.
12. The method according to any one of claims 1-10 wherein the particulate material comprises particles
- 30 having a spectrum of diameters.
13. The method according to either claim 11 or claim 12 wherein at least some of the particles have diameters within a range from 1 nanometer to 1 micrometer.

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14. The method according to either claim 11 or claim 12 wherein at least some of the particles have diameters within a range from 1 nanometer to 100 nanometers.
15. The method according to claim 11 wherein substantially all particles have diameters within a range from 1 nanometer to 500 micrometers.
16. The method according to either claim 11 or claim 12 wherein the particles have a primary particle diameter in a range from 5 nanometers to 50 nanometers.
17. The method according to either claim 11 or claim 12 wherein the particles have an average particle size in a range from 5 nanometers to 20 nanometers.
18. The method according to either claim 11 or claim 12 wherein the average particle size is about 15 nanometers.
19. The method according to any one of the preceding claims wherein the method includes a further step prior to step (d), the step comprising mixing a polymer component into the gel, the polymer component being capable of bonding with the gel and particulate material during step (d).
20. The method according to claim 19 wherein the polymer material is either hydrophobic or rendered hydrophobic during step (d).
21. The method according to any one of the preceding claims wherein the method includes a further step prior to step (d), the further step comprising adding a surface modifier to the gel, the surface modifier being capable of increasing the intrinsic chemical hydrophobicity of a hydrophobic surface formed with the modified gel.
22. The method according to claim 21 wherein the surface

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modifier further enhances bonding between the particulate material and the gel.

23. The method according to either claim 21 or claim 22 wherein the surface modifier is a compound including one or more hydrophobic groups and one or more condensation cure groups.

5 24. The method according to claim 23 wherein the one or more hydrophobic groups include one or more of the following groups:

10 methyl;

ethyl;

vinyl;

trifluoropropyl.

25. The method according to either claim 23 or claim 24 wherein the one or more condensation cure groups include one or more of the following groups:

15 acetoxy;

enoxy;

oxime;

20 alkoxy;

amine.

26. The method according to any one of the preceding claims wherein the particulate material comprises a flame-hydrolysed silica powder, and the gel comprises 25 a silicon dioxide gel.

27. The method according to any one of the preceding claims in combination with claim 19 wherein the polymer component comprises polydimethylsiloxane (PDMS).

30 28. A method of forming a coating on a substrate, comprising the steps of:
- forming a modified gel in accordance with the method of any one of the preceding claims;

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- applying the modified gel to the substrate; and
 - treating the applied modified gel such that a coating is formed on the substrate, the coating having a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface hydrophobicity, such that water forms a contact angle of at least 150°.
- 5 29. The method according to claim 28 wherein the hydrophobic surface of the coating is such that water forms a contact angle on it of at least 155°.
- 10 30. The method according to claim 28 wherein the hydrophobic surface is such that water forms a contact angle on it of at least 160°.
- 15 31. The method according to claim 28 wherein the hydrophobic surface is such that water forms a contact angle on it of at least 165°.
- 20 32. The method according to any one of claims 1-31 wherein the modified gel is in the form of a slurry.
- 25 33. The method according to any one of claims 28-32 wherein the step of applying the modified gel to the substrate comprises using one of the following techniques:
spin coating;
dip coating; or
spray coating.
- 30 34. The method according to any one of claims 28-33 wherein the step of treating the mixture comprises drying the applied modified gel such that a solid coating is formed.
35. The method according to claim 34 wherein the step of drying includes a step of heating the applied modified gel to a temperature which is sufficient to evaporate any solvents.

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36. The method according to either claim 34 or claim 35 wherein the step of drying the coating comprises heating the coating to a temperature in the range from 120° to 400°C.
- 5 37. A modified gel produced by a method in accordance with any one of claims 1-27.
38. An object having a surface, at least a portion of which is coated with a hydrophobic coating formed from a modified gel made by a method in accordance with any one of claim 1-27.
- 10 39. A hydrophobic coating produced by a method in accordance with any one of claims 28-36.
40. An object having a surface, at least a portion of which is coated with a hydrophobic coating produced by a method in accordance with any one of claims 28-
- 15 36.
41. A method of forming a material capable of being applied to surface, substantially as herein described with reference to the accompanying examples and Figures.
- 20 42. A method of forming a coating on a substrate substantially as herein described with reference to the accompanying examples and Figures.

25

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/00993

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. ?: C09K 3/18, C09D 5/00, 5/08, 5/16, 183/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
IPC: AS ABOVE

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT & JAPIO (Search terms: gel, silica)**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent abstract Accession No. 98-351631/31, Class A89 G02 L01, JP 10133002A (CANON KK) 22 May 1998. See abstract	1-42
X	Derwent abstract Accession No. 93-162242/20, Class P81, JP 05093170A (MITSUBISHI RAYON CO LTD) 16 April 1993 See abstract	1-42
X	EP 0381376A (SHIN-ETSU CHEMICAL CO LTD) 8 August 1990. See column 2 lines 18-49, column 5 lines 28-57, Examples 1-4 and claim 1.	1-42

Further documents are listed in the continuation of Box C See patent family annex

* Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search

6 September 2000

Date of mailing of the international search report

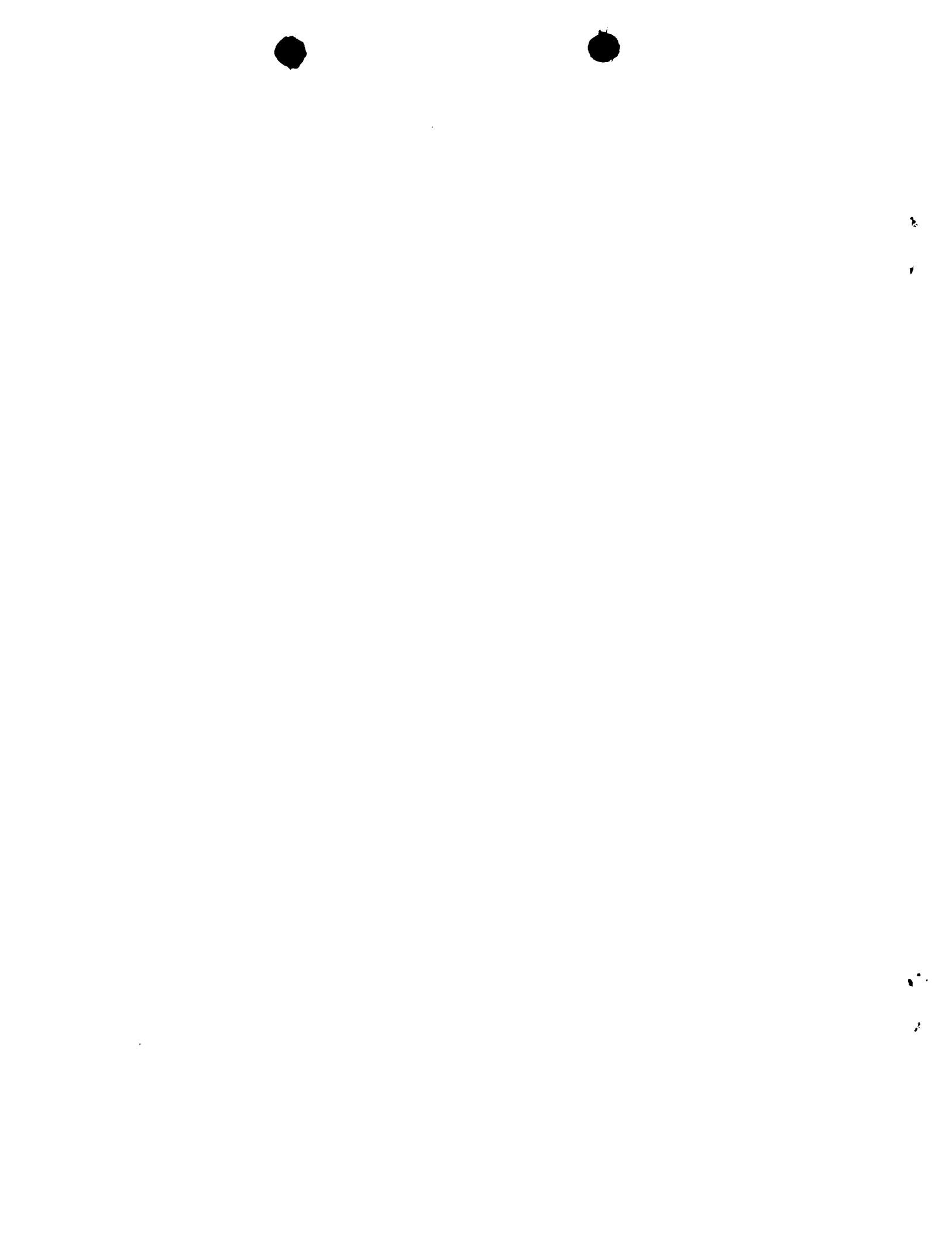
11 SEP 2000

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/00993

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0430156A (TOSHIBA SILICONE CO LTD) 5 June 1991 See page 5 lines 13-24, page 6 lines 51-58 and page 9 lines 39-42	1-42
A	Derwent abstract Accession No. 93-049877/06, Class A32 G02 M13, JP 05001391A (TOA GOSEI CHEM IND LTD) 8 January 1993 See abstract	1-42



INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/00993

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member				
JP	10133002A	NONE					
JP	05001391A	NONE					
EP	0381376A	DE	69003121	JP	2196859	US	5045574
EP	0430156A	DE	69016609	US	5091460	JP	2574061
JP	05001391A	NONE					

END OF ANNEX



- 2 -

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25 (d) treating the mixture such that a modified gel is formed in which the particulate material is bound to the gel, and the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 150°.

30 In a second aspect, the present invention provides a method of forming a coating on a substrate, the method including steps (a) to (d) of the first aspect of the present invention, and further including the steps of:

